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Preface

The *Space Programs Summary* is a six-volume, bimonthly publication that documents the current project activities and supporting research and advanced development efforts conducted or managed by JPL for the NASA space exploration programs. The titles of all volumes of the *Space Programs Summary* are:

- Vol. I. The Lunar Program (Confidential)
- Vol. II. The Planetary-Interplanetary Program (Confidential)
- Vol. III. The Deep Space Network (Unclassified)
- Vol. IV. Supporting Research and Advanced Development (Unclassified)
- Vol. V. Supporting Research and Advanced Development (Confidential)
- Vol. VI. Space Exploration Programs and Space Sciences (Unclassified)

The *Space Programs Summary*, Vol. VI consists of an unclassified digest of appropriate material from Vols. I, II, and III; an original presentation of technical supporting activities, including engineering development of environmental-test facilities, and quality assurance and reliability; and a reprint of the space science instrumentation studies of Vols. I and II.



W. H. Pickering, Director
Jet Propulsion Laboratory

Space Programs Summary No. 37-35, Volume V

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PROPULSION DIVISION

I. Solid Propellant Engineering

A. High-Energy Propellant Development

F. A. Anderson and L. Hiraoka

The high-energy propellant development effort involving hydrazine dperchlorate (HP_2), which has been reported in several previous *Space Programs Summaries*, is continuing in essentially two separate phases. One is the study and characterization of HP_2 itself, the other is the propellant development effort which includes binder development, compatibility studies, etc. Two basic binder systems have been considered: one is a carboxyl terminated hydrocarbon polymer, the other is a low oxygen content polyester, also with terminal carboxyl groups.

1. Performance Potential

Theoretical performance calculations have been made for hydrazine dperchlorate oxidizer (HP_2) in the two binder systems being considered, and a comparison made of the maximum performance potential of both. Fig. 1 is a plot of the specific impulse as a function of the percent oxidizer in each of the binders. The polyester polymer

is a carboxy terminated polyester containing 22.8% oxygen in the polymer. The CTPB binder is a carboxy terminated polybutadiene polymer. As may be seen in Fig. 1 the maximum I_{sp} (260.4 sec) of the polyester system is lower than the maximum for the CTPB system (263.0 sec) by 2.6 sec of impulse. However, up to an oxidizer loading of approximately 84% the performance of the polyester

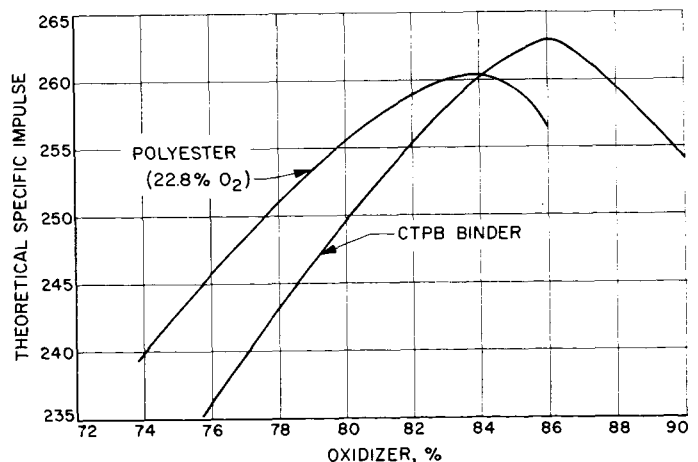
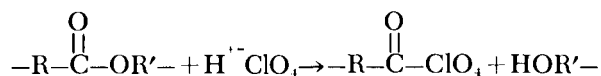


Fig. 1. Theoretical specific impulse of HP_2 /binder systems

system is the higher of the two. Therefore, processing problems may dictate the final binder system selection. The viscosity of the CTPB polymer is considerably greater than that of the polyester and at this time it appears unlikely that satisfactory processing can be accomplished with the CTPB system at oxidizer loadings above 84%. Some incompatibility problems at elevated temperatures have been encountered with both binders, and studies are in progress which will attempt to understand and remedy the incompatibility.

2. Compatibility Studies

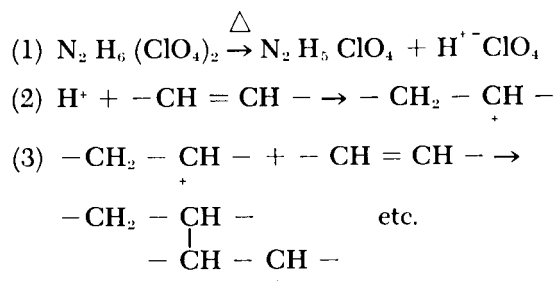
Dry HP₂ can be mixed into both the CTPB and the polyester polymers and stored at room temperature under dry atmosphere for several days without any visible change or effect taking place. Samples have been stored in this way for a week or more with no apparent incompatibility occurring. However, when these mixtures are subjected to elevated temperatures, such as a 140°F curing temperature, the HP₂/CTPB mixture becomes nearly black in color and cures to a hard brittle mass. This occurs in the absence of any curing agent. The HP₂/polyester mixture discolors slightly. Also, the viscosity appears to decrease with time, accompanied by an odor suggestive of an ether. No curing takes place however with the polyester system. Tests were conducted by heating mixtures of HP₂ and various polymers containing one or more of the following groups: carboxyl, hydroxyl, ester, and olefinic. In each case where olefinic groups were present in the polymer, and only when olefinic groups were present, a hard cure resulted, leading to the conclusion that a reaction occurs with the double bond causing a cross-linking of the polymer whereas no curing or cross-linking occurs with the other reactive groups on the polymer chain. Further support for this conclusion lies in the results obtained from heating CTPB polymer mixed with various acids and oxidizers. An explanation for the effect observed with the HP₂/polyester mixes is that quite probably a hydrolysis of the ester by the perchloric acid is taking place as follows:



In addition to the hydrolysis, oxidation of groups in the polymer may also be taking place yielding, among other things, ketones. This would account for the decrease in viscosity as well as the odors.

When 15% perchloric acid (HClO₄) was mixed with CTPB polymer and this mixture stored at 140°F for 4 days a hard rubbery material resulted. The same type of

cured material resulted from a mixture of sulfuric acid (H₂SO₄) and CTPB polymer. A higher temperature (250°F) was required for the sulfuric acid cure. Both of these acids can supply a hydronium ion. However, when CTPB polymer was heated at various temperatures with materials such as NH₄ClO₄, which could supply a perchlorate ion, no reaction was observed. These results strongly suggest that the hard cure of the CTPB polymer experienced at elevated temperatures is due to the activity of a hydronium ion. In the case of the HP₂/CTPB mixture, the hydronium ion would be supplied by perchloric acid which is produced as a result of slow decomposition of the HP₂ at the curing temperature. It is important to note that no cure or discoloration occurs with either HP₂ sulfuric acid, or perchloric acid in CTPB polymer in one week's storage at room temperature. It is therefore hypothesized that at the cure temperature of 140°F, the HP₂ undergoes some decomposition which yields perchloric acid. The perchloric acid then supplies hydronium ions which react with the polymer causing the hard cure. These reactions can be illustrated as follows:



By infrared studies, an attempt has been made to further define the reactions taking place between the HP₂ and the polymer. These results are inconclusive at this time.

3. Stabilization of HP₂ in Polymer

As a result of the incompatibility problem between HP₂ and polymer explained above, an effort has been made to solve this problem. One approach is to pacify or stabilize the HP₂. A number of compounds were investigated as to their stabilizing effect, and N-phenyl-beta-naphthylamine (PBNA) was found to be quite effective. PBNA is used rather extensively in the polymer and rubber industry as an antioxidant. The effectiveness of the PBNA appears to be strongly dependent on its particle size and the method of incorporating it into the HP₂/CTPB mix. Samples prepared by tumbling HP₂ with 1% PBNA so as to effect good blending, followed by mixing with CTPB polymer, have remained stable up to 8 days at 140°F

—stable here means no apparent reaction or cure taking place. However, when 1% PBNA was first mixed into the polymer and then the HP₂ alone added, hard cures resulted in 24 hr at 140°F. It appears that the finely powdered PBNA coats the HP₂ particles and thereby, by some mechanism, stabilizes the system. Unfortunately PBNA is soluble in many of the curing agents which have been investigated for this system. If the PBNA-coated HP₂ is mixed into a binder system containing a curing agent in which the PBNA is soluble, the stabilizing effect is lost. An immediate problem is to discover either an effective stabilizer which is insoluble in the curing agents presently used, or a satisfactory curing agent in which the PBNA is not soluble. Table 1 lists a number of potential curing agents which have been investigated for this system and shows whether or not PBNA is soluble in each material. The list includes a few additional materials which would not be considered as curing agents per se.

B. High-Energy Solid Propellant Development: B-N-H

R. A. McKay and D. E. Udlock

The PEH-H₃D propellant (Ref. 1) invented by American Cyanamid Company is one of three (SPS 37-20, Vol. V, pp. 30-34) selected by JPL for evaluating the practicality of B-N-H solid propellants. At the time of selection, the propellant was rated as nearly ready for a development program leading to a high-performance motor for space application. Thus the investigation was to be carried out on a scale suitable for both propellant and motor development. As part of this plan, sufficient ingredients were obtained for 210 lb of propellant.

A small mixer facility was designed and constructed to serve the process needs of this program. A full description of the equipment will be released later. The facility permits the remote processing of castable propellants from the condition of ingredients suitably arranged in hoppers, to finished propellant cast into receivers. Features include atmosphere and temperature control, mixer speed control, and appropriate instrumentation including television. Because of the closed system characteristics this equipment is adaptable for processing toxic materials such as beryllium, or moisture-sensitive materials such as nitronium perchlorate or hydrazinium diperchlorate.

Table 1. Solubility of PBNA

Reagent	Chemical formula	Solubility ^a
MAPO		YES
EPON X-801		YES
ERLA-0510		YES
UNOX-221		YES
DER 332 LC		YES
DETA	$\text{NH}_2-\text{CH}_2-\text{CH}_2-\text{NH}-\text{CH}_2-\text{CH}_2-\text{NH}_2$	YES
ETHYLENE GLYCOL	$\text{HO}-\text{CH}_2-\text{CH}_2-\text{OH}$	SLIGHTLY
GLYCEROL		NO
1,2,4-BUTANETRIOL		NO
1,2,6-HEXANETRIOL		NO
N-HEXANE	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$	NO
15% PERCHLORIC ACID	$\text{HClO}_4 \text{ (AQ)}$	NO

^a Solubility test consisted of mixing approximately 20 mg of PBNA with 2 ml of reagent.

1. Ingredient Status: H_3D

Important in formulating propellant is knowledge of the elemental analysis of each ingredient. The H_3D on hand was packaged under methanol to reduce hazards in handling and to improve its shelf life. During storage gas evolution from the salt cake was observed and reported in SPS 37-27, Vol. V. Melting point determinations indicated that the material was still of good purity, but this was not confirmed by elemental analysis. The H_3D was made by the removal of one hydrazine from H_4D ; removal of a second hydrazine yields H_2D . If the ingredient is a plausible mixture of the salts it should be evident from the elemental analysis. The data so far do not correspond to a mixture of salts but suggest the presence of other compounds.

Continuing studies have shown that the preparatory drying procedures need improvement. The present procedure consists of suction filtration, next removing the bulk of the remaining solvent at room temperature under dry nitrogen, and then finishing at 60°C, also under dry nitrogen. The former procedure of drying at 60°C in an air-vented oven has been discontinued. It was shown that material dried under dry nitrogen or anhydrous air will pick up a small amount of methanol if carried by air at 55-60°C and greater amounts (approximately 1.5%) of water from ambient air. It was also observed that still greater amounts of methanol may be retained within clumps when the material is dried in bulk on trays. This may explain the presence of carbon detected by some of the elemental analyses. In the case of tray-drying, the crystals stuck together as the solvent evaporated, sometimes producing lumps which required considerable force to break. Accordingly, the present procedure includes the use of a tumble dryer for the room temperature step of the drying. Tests made with a preliminary model dryer, using a dry nitrogen sweep, yielded a free-flowing granular material which required no further treatment. Additional tests are proceeding in order to determine suitable drying times and to evaluate the quality and composition of the material so prepared.

2. Ingredient Status: PEH

The elemental analyses of PEH for C, N, and H sum to less than 100% and were shown to exhibit variation within sample lots. Additional work, including more detailed analysis, is proceeding.

3. Propellant Processing

Propellant processing has commenced utilizing the American Cyanamid AC-2a formulation. This formulation consists of equimolar amounts of H_3D , PEH, and hydrazine, with an added 1 wt % of aniline to serve as plasticizer. In our process, pending improved ingredient identification, the weight of H_3D was based on the boron content, the weight of PEH was based on the nitrogen content, and hydrazine was added to give BN stoichiometry. This formulation will serve throughout the present phase of the program.

As a check on the compatibility of the present ingredients prior to processing on a larger scale in the so-called small mixer facility, a 5-g preliminary propellant batch was made in glassware using simple benchtop procedures. No unexpected problems were encountered. An impact sensitivity of about 10 in. with a 2-kg weight was measured with the JPL impact tester by the Bruceton method. Processing was then moved to the remotely operated 1-pint mixer. Six batches have been attempted. The third batch was terminated when one of the ingredients failed to leave a hopper, and the sixth batch was terminated when trouble was detected in the mixer head. The hopper problem was solved by a change in preparation of the ingredient; the mixer problem is believed solved with redesigned seals separating the mixing and gearhead zones. From the other four batches there evolved a technique to cast specimens for burning rate and density measurements using plastic drinking straws as molds.

4. Propellant Density

As was expected, this study demonstrated that the density of the propellant is influenced significantly by processing conditions, especially pressure. Propellant density, as cast, varied from 1.109 g/cm³ in the first batch to 0.998 g/cm³ in the second. Bubbles arising in H_3D upon melting, as discussed in SPS 37-27, Vol. V, and shrinkage during the freezing of the propellant both influence the bulk density. So also does gas evolution from decomposition.

Samples from the first two batches were centrifuged at about 240 g for 1 hr at 87 to 93°C to check the possibility of achieving bubble-free propellant (melting point 72°C). Both samples became clear and amber, as compared with the opaque white appearance normally exhibited. Moreover, the samples supercooled to room temperature without apparent change. Examination under a binocularscope showed that some of the relatively small

remaining bubbles occurred as chains, thus verifying that decomposition does take place in the melt. In the supercooled state, the samples had densities of 1.091 and 1.092 g/cm³, respectively. Within 3 hr, both samples had started to recrystallize. Subsequent density determinations with these samples were not attempted because of voids formed during crystallization. (The casting hardware for motor preparation was designed to prevent such void formation.) Additional tests using centrifugation are under way, with the crystallization step to take place under isoöctane in an attempt to determine a practical maximum propellant density of the selected formulation.

5. Burning Rate

Propellant burning rate should correlate with propellant density and in the few tests made so far this correlation was observed. The best specimens were cast from the fifth batch which had a density of 1.077 g/cm³. Some of the specimens, as well as most of the earlier ones, were

damaged by leakage of the molds. The preliminary data include a burning rate of 0.202 in./sec at 100 psia. Two samples of practically bubble-free supercooled propellant prepared from the same batch by centrifugation gave burning rates of 0.276 and 0.273 in./sec. These data led to the conclusion that motor testing of supercooled propellant would probably offer no advantages.

6. Future Plans

Development operations will continue in an attempt to produce propellant with density as close to maximum, and burning rate as close to minimum, as possible. Then, relying upon the resulting process information and the burning rate versus pressure data, test motors will be loaded and fired. Meanwhile, work to characterize the ingredients will continue with the assistance of the analytical services of Dynamic Science Corporation, Monrovia, California.

Reference

1. *ARPA Project Principia*, Contract NOrd 18728, American Cyanamid Company Stamford, Connecticut, (Confidential).